Interfaces

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I N T E R F A C E S

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Abstract

Several aspects of the theory of the coexistence of phases and equilibrium forms are discussed. In section 1, the problem is studied from the point of view of thermodynamics. In section 2, the statistical mechanical theory is introduced. We consider, in particular, the description of the microscopic interface at low temperatures and the existence of a free energy per unit area (surface tension). In section 3, a proof is given of the microscopic validity of the Wulff construction in a simplified model of a two-dimensional interface. Finally, in section 4, the roughening transition and the formation of facets in an equilibrium crystal are studied. Appendices A and B concern, respectively, the first and second points of section 2, mentioned above.

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1 Introduction

When a fluid is in contact with another fluid, or with a gas, a portion of the total free energy of the system is proportional to the area of the surface of contact, it is also proportional to a coefficient, the surface tension, which is specific for each pair of substances. Equilibrium, which is the condition of minimum free energy in the system, will accordingly be obtained by the utmost possible reduction of the surfaces in contact.

We must understand here, not an absolute but a relative minimum, depending on the material circumstances of the case that is considered. Mathematicians restrict the term minimal surfaces to the former cases, or more generally, to all cases in which the mean curvature is zero. Other surfaces which are only minimal with respect to the volume contained, are called surfaces of constant mean curvature. From the fact that we may extend a soap film across any ring of wire, however the wire be bent, we see that there is no end to the variety of the minimal surfaces that can be constructed or imagined. To fit a minimal surface to the boundary of any given closed curve in the space is a problem formulated by Lagrange, commonly known as the problem of Plateau, who solved it with the soap films.

When we have three fluids in contact with one another, new interesting situations arise. Suppose that a drop of some fluid, a, float on another fluid, b, while both are exposed to air, c. Then we have three different surfaces of contact, and the total free energy of the system consists of three parts, associated to these three surfaces. Equilibrium will be reached by contracting the surfaces whose surface tension happens to be large and extending those where it is small. A drop of fluid a, will exist provided its own two surface tensions exceed the surface tension between fluid b and the air, i.e., provided that

$$\tau_{ab} + \tau_{ac} > \tau_{bc}$$

If equality is attained, then a film of fluid a is formed, a situation which is known as perfect wetting. For instance, floating on water, turpentine gathers into a drop and olive oil spreads out in a film.

When one of the substances involved is anisotropic, such as a crystal, the equilibrium is not determined as it was in the case of a fluid, by the condition of minimal area. The contribution to the total free energy of each element of area of the crystal surface depends on its orientation with respect to the crystalline axes.

Gibbs' article "On the equilibrium of heterogeneous substances" (Gibbs 1875) is a theoretical system of thermodynamics, of nearly 300 pages, derived from the first and second law. In this work, Gibbs introduced the principle of minimum of total surface free energy. He also showed the role of the anisotropic surface tension for determination of the shape of a crystal in equilibrium. Concerning the formation of facets, he remarks:

> "the value of τ varies greatly with the direction of the surface with respect to the axes of crystallization and in such a manner as to have sharply defined minima (The differential coefficients of τ with respect to the direction-cosines of the surface appear to be discontinuous functions of the latter quantities)."

He also points out the complexities of actual growth of a crystal and suggests that only small crystals have an ideal equilibrium form:

> "it seems not improbable that the form of very minute crystals in equilibrium is principally determined by the condition that the free energy shall be a minimum for the volume of the crystal, but as they grow larger the deposition of new matter on the different surfaces will be determined more by the nature (orientation) of the surface and less by their size in relation to the surrounding surfaces. As a final result, a large crystal thus formed will generally be bounded by those surfaces alone on which the deposition of new matter takes place least readily"

Curie (1885) considered also, independently of Gibbs and using a different method, a crystal in equilibrium with its own vapor phase, arriving at the same conclusion. For a crystal of N faces, of area F_i and specific surface free energies τ_i, he found that

$$f = \tau_1 F_1 + \tau_2 F_2 + \ldots + \tau_N F_N$$

has the minimum value for a given volume. As an application he examined two problems, a crystal taking the form of a parallelepiped, and a crystal taking the form of a of a cubo-octahedron. The second problem, for which Curie gives only the result, is not obvious.

The article by Curie was the point of departure for Wulff's classical experiments on crystal growth. He reported the results in a paper (Wulff 1901), first published in Russian in 1895. His principal conclusions include the celebrated Wulff's theorem on the shape of the equilibrium crystal:

> "The minimum surface energy for a given volume of a polyhedron will be achieved if the distances of its faces from one and the same point are proportional to their capillary constants."

The term capillary constants was used for the surface tension. Denoting these distances by h_i, this means that

$$\frac{h_1}{\tau_1} = \frac{h_2}{\tau_2} = \cdots = \frac{h_N}{\tau_N}$$

Wulff himself supported his principle mainly by its consequences (relating the rate of growth in various directions to the corresponding surface tensions). His attempt at a general proof failed. He surmised that the surface free

energy f (given by Curie's formula) and the volume V are related to h_i by the following expressions

$$f = p \sum \tau_i h_i^2, \quad V = q \sum h_i^3$$

where p and q are constants. However, the simplest example of a parallelepiped contradicts these statements.

The complete proof of Wulff theorem was presented by von Laue (1943), Herring (1951), and others.

The surfaces tensions are dependent upon the geometric distribution of the particles making up the crystal structure. In this way the Wulff theorem establish a relation between the forms and the structure of crystals. Although it is not easy to find equilibrium crystals in nature we may think, following Schneer (1970), that the ensemble of the forms of a mineral species should approach equilibrium. The distribution of these forms in geological time and space is the outcome of a world-experiment establishing the probability of occurrence of each particular form.

A complete map of the mineral kingdom known to science was presented in Goldschmidt Atlas (1913–1923). Each of the nine volumes of illustrations was accompanied by a volume of morphological data. Ironically, the first volume of the Atlas appeared in 1913, one year after the discovery of X-ray difraction. Its purpose was to provide data for the determination of the molecular forces within the crystal from the crystal form.

It is only in recent times that equilibrium crystals have been produced in the laboratory. Most crystals grow under non-equilibrium conditions, as predicted by Gibbs, and is a subsequent relaxation of the macroscopic crystal that restores the equilibrium. This requires transport of material over long distances and the time scales can be very long, even for very small crystals. On has been able to study, however, metal crystals in equilibrium of size 1–10 micron (Heyraud and Metois 1980, 1983). Equilibration times of a few days were observed.

A very interesting phenomenon that can be observed on equilibrium crystals is the roughening transition. This transition is characterized by the disappearance of a facet of a given orientation from the equilibrium crystal, when the temperature attains a certain particular value. Roughening transitions have been found experimentally, first, in negative crystals, i.e., vapor bubbles included in a crystal, in organic substances (Pavlovsca and Nenov 1971, 1973). The best observations have been made on helium crystals in equilibrium with superfluid helium (Balibar and Castaign 1980, 1985, Keshishev et al. 1981, Wolf et al. 1983), since the transport of matter and heat is extremely fast in the superfluid. Crystals grow to size of 1–5 mm and relaxation times vary from milliseconds to minutes. Roughening transitions for three different types of facets have been observed.

1 Thermodynamics of equilibrium forms

1.1 Variational problem

Our aim is to find the shape of a droplet of a phase c, the crystal, inside a phase m, called the medium, when both phases are in equilibrium. The phase c need not be a crystal, this terminology is adopted to stress that we consider that c has anisotropic properties. This shape is obtained by minimizing the surface free energy between the phases c and m.

Let $\mathbf{n}$ be a unit vector in $\mathbf{R}^d$ and consider the situation in which the phases c and m coexist over a hyperplane perpendicular to $\mathbf{n}$, we denote by $\tau(\mathbf{n})$ the surface tension, or free energy per unit area, of such an interface. We consider the surface tension $\tau(\mathbf{n})$ as a positive function on the unit sphere $\mathbf{S}^{d-1} \subset \mathbf{R}^d$, but we do not require now the symmetry $\tau(\mathbf{n}) = \tau(-\mathbf{n})$. In the case under consideration $\tau(\mathbf{n})$ is obviously a symmetric function, but non-symmetric situations are also physically interesting and they appear, for instance, in the case of a sessile drop on a wall to be be discussed in section 1.6.

We denote by B the set of $\mathbf{R}^d$ occupied by the phase c, and by ∂B the boundary of B. The total surface free energy of the crystal is given by

$$\tau(\partial B) = \int_{\xi \in \partial B} \tau(\mathbf{n}(\xi)) ds_\xi \tag{1.1}$$

Here $\mathbf{n}(\xi)$ is the exterior unit normal to ∂B at ξ and ds_ξ is the element of area at this point. We suppose that the boundary of B is sufficiently smooth so that the normal is defined for almost all s in ∂B.

The variational problem is to minimize (1.1) under the constraint that the total (Lebesgue) volume $|B|$ occupied by the phase c is fixed. Given a set $\mathcal{W}$, we say that the crystal B has shape $\mathcal{W}$ if after a translation and a dilation it equals $\mathcal{W}$. The solution of the variational problem, known under the name of Wulff construction, is given below. Notice that the problem is scale invariant, so that if we can solve it for a given volume of the phase c, we get the solution for other volumes by an appropriate scaling. Let $\mathcal{W}$ be defined by

$$\mathcal{W} = \{\mathbf{x} \in \mathbf{R}^d : \mathbf{x} \cdot \mathbf{n} \leq \tau(\mathbf{n})\} \tag{1.2}$$

where the inequality is assumed for every $\mathbf{n} \in \mathbf{S}^{d-1}$ ($\mathbf{x} \cdot \mathbf{n}$ denotes the euclidean scalar product). We shall show that this set, which will be called the Wulff shape, gives the optimal shape for the crystal.

Theorem 1.1. *Let $\mathcal{W}$ be the Wulff shape (1.2) for the surface tension function $\tau(\mathbf{n})$. Let $B \subset \mathbf{R}^d$ be any other region with sufficiently smooth boundary and the same (Lebesgue) volume as $\mathcal{W}$. Then*

$$\tau(\partial B) \geq \tau(\partial \mathcal{W}) \tag{1.3}$$

with equality if and only if B and $\mathcal{W}$ have the same shape.

A proof of this Theorem, based on some version of the isoperimetrical inequality, will be given at the end of section 2.2 (in this proof we follow Taylor 1987).

We now state some elementary properties of $\mathcal{W}$. Being defined in (1.2) as the intersection of closed half-spaces the Wulff shape $\mathcal{W}$ is a closed, bounded convex set, i.e., a convex body.

Among the functions $\tau(\mathbf{n})$, which through (1.2) define the same shape $\mathcal{W}$, there is a unique function having the property that all planes $\{\mathbf{x} \in \mathbf{R}^d : \mathbf{x} \cdot \mathbf{n} = \tau(\mathbf{n})\}$, associated to all different unit vectors $\mathbf{n}$, are tangent to the convex set $\mathcal{W}$. This function is given by

$$\tau_{\mathcal{W}}(\mathbf{n}) = \sup_{\mathbf{x} \in \mathcal{W}} (\mathbf{x} \cdot \mathbf{n}) \tag{1.4}$$

and is called the support function of the convex body $\mathcal{W}$. If we consider an arbitrary function $\tau(\mathbf{n})$ defining the Wulff shape $\mathcal{W}$, it can be that some of these planes do not touch the set $\mathcal{W}$. In other words, we have always

$$\tau(\mathbf{n}) \geq \tau_{\mathcal{W}}(\mathbf{n}) \tag{1.5}$$

but the inequality sign can hold for some $\mathbf{n}$. The support function $\tau_{\mathcal{W}}(\mathbf{n})$ is the smallest function on the unit sphere which gives the Wulff shape $\mathcal{W}$.

1.2 Geometric inequalities

We can state as follows the isoperimetric property of convex bodies.

Theorem 1.2. *Let $\mathcal{W} \subset \mathbf{R}^d$ be a convex body and $\tau_{\mathcal{W}}(\mathbf{n})$ the corresponding support function. For any set $B \subset \mathbf{R}^d$, with sufficiently smooth boundary, we have*

$$\tau_{\mathcal{W}}(\partial B) \geq d\ |\mathcal{W}|^{1/d} |B|^{(d-1)/d} \tag{1.6}$$

where $|\mathcal{W}|$, $|B|$, denote the (Lebesgue) volumes of $\mathcal{W}$, B, respectively, and $\tau_{\mathcal{W}}(\partial B)$ is the surface functional defined by (1.1). The equality occurs only when B and $\mathcal{W}$ have the same shape.

Let us recall the following classical statement, known as the isoperimetric property of the circle.

Proposition. The area F and the length L of any plane domain with rectifiable boundary satisfy the inequality

$$L^2 \geq 4\pi F \tag{1.7}$$

The equality sign holds only for the circle.

If for the set $\mathcal{W}$ we choose D, the closed circle of unit radius with center at the origin, then the corresponding support function $\tau_{\mathcal{D}}(\mathbf{n})$ is equal to the constant 1, and we obtain the isoperimetric property.

Mathematicians were convinced that the isoperimetric property of the circle is valid since ancient times. The known proofs of inequality (1.7) may be grouped together around several main approaches. Three of them go back to Steiner, who gave the first non rigorous proofs of the isoperimetric property of the circle on the plane and of the sphere and proved a similar property of the ball in space.

We shall describe here another approach based on the notion of vector addition of sets due to Minkowski. This is a very general approach which easily leads to the Brunn-Minkowski inequality and, as a particular case, to the isoperimetric inequality.

To every pair of non-empty sets $A, B \subset \mathbf{R}^d$ their vector Minkowski sum is defined by $A + B = \{a + b : a \in A, b \in B\}$. If A, B are compact sets, then $A + B$ is compact. In this case each of the sets necessarily has a volume, its Lebesgue measure. The following Theorem is known as the Brunn-Minkowski inequality.

Theorem 1.3. *For non empty compact sets $A, B \subset \mathbf{R}^d$*

$$|A + B|^{1/d} \geq |A|^{1/d} + |B|^{1/d} \tag{1.8}$$

and the equality sign in (1.8) holds only in the following cases: $|A + B| = 0$, one of the sets A, B consists of a single point, and A and B are two convex bodies with the same shape.

A proof of this Theorem can be found in the book by Burago and Zalgaller (1988). First one proves by direct computation that the inequality holds in the case in which A and B are parallelepipeds with sides parallel to the coordinate axis. The validity of the inequality is then extended by induction to all finite unions of such parallelepipeds and, finally, to all compact sets by an appropriate limit process.

The following geometrical remark will next be used to prove the isoperimetric inequality.

Remark. Let $\mathcal{W}$ be a convex body in $\mathbf{R}^d$. Given any set $B \subset \mathbf{R}^d$, with sufficiently smooth boundary, we can express the functional $\tau_{\mathcal{W}}(\partial B)$ as

$$\tau_{\mathcal{W}}(\partial B) = \lim_{\lambda \to 0} \frac{|B + \lambda \mathcal{W}| - |B|}{\lambda} \tag{1.9}$$

where $\lambda \mathcal{W}$ denotes the homothetic set $\{\lambda \mathbf{x} : \mathbf{x} \in \mathcal{W}\}$. If $B \subset \mathbf{R}^d$ is bounded, the functional $\tau_{\mathcal{W}}$ is well defined. In particular, (1.9) shows that

$$\tau_{\mathcal{W}}(\partial \mathcal{W}) = d\,|\mathcal{W}| \tag{1.10}$$

Proof of Theorem 1.2. We first prove equation (1.9). In fact, if $H(\mathbf{n})$ denotes the half space whose oriented unit normal is $\mathbf{n}$, we obtain from the definition of $\tau_{\mathcal{W}}$

$$\tau_{\mathcal{W}}(\mathbf{n}) = \operatorname{dist}\big(\partial H(\mathbf{n}), \partial(H(\mathbf{n}) + \mathcal{W})\big) \tag{1.11}$$

We may then write

$$\begin{aligned}\tau_{\mathcal{W}}(\partial B) &= \int_{\xi\in\partial B} \operatorname{dist}\big(\partial H(\mathbf{n}(\xi)), \partial(H(\mathbf{n}(\xi)) + \mathcal{W})\big) ds_\xi \\ &= \int_{\xi\in\partial B} \lim_{\lambda\to 0}(1/\lambda) \operatorname{dist}\big(\xi, \partial(B + \lambda\mathcal{W})\big) ds_\xi \end{aligned} \tag{1.12}$$

This last expression coincides with the right hand side of (1.9), and proves the validity of this equation.

Then inequality (1.6) follows by applying the Brunn-Minkowski inequality to $|B + \lambda\mathcal{W}|$. This gives

$$|B + \lambda\mathcal{W}| - |B| \geq \big(|B|^{1/d} + \lambda|\mathcal{W}|^{1/d}\big)^d - |B| \geq d\,\lambda\,|B|^{(d-1)/d}|\mathcal{W}|^{1/d} \tag{1.13}$$

which, taking equation (1.9) into account, ends the proof of inequality (1.6).

By taking limits we can deduce (1.6) from (1.8). However, conditions for the equality to occur in (1.6) cannot be found in this manner. For a proof that $\mathcal{W}$ is the unique minimum see Burago and Zalgaller (1988).

Proof of Theorem 1.1. The proof can be obtained as a consequence of the Theorem 1.2. Let $\mathcal{W}$ be the Wulff shape corresponding to the function τ. Then

$$\tau(\partial B) \geq \tau_{\mathcal{W}}(\partial B) \geq d\ |\mathcal{W}|^{1/d}|B|^{(d-1)/d} \tag{1.14}$$

taking into account equation (1.9) and the isoperimetric inequality (1.6). But, when $B = \mathcal{W}$, we have

$$\tau(\partial\mathcal{W}) = \tau_{\mathcal{W}}(\partial\mathcal{W}) = d\ |\mathcal{W}| \tag{1.15}$$

The first equality in (1.15) follows from the fact that $\tau_{\mathcal{W}}(\mathbf{n}) \neq \tau(\mathbf{n})$ only for the unit vectors $\mathbf{n}$ for which the planes $\mathbf{x}\cdot\mathbf{n} = \tau(\mathbf{n})$ are not tangent to the convex set $\mathcal{W}$. The second equality follows from equation (1.9). Therefore

$$\tau(\partial B) \geq \tau(\partial\mathcal{W})\,(|B|/|\mathcal{W}|)^{(d-1)/d} \tag{1.16}$$

which, when $|B| = |\mathcal{W}|$, gives the stated inequality (1.3). The equality in (1.3) corresponds to the equality in (1.6). The Theorem is proved.

1.3 Convexity properties

It is expected, from thermodynamic reasons, that the surface tension $\tau(\mathbf{n})$ is equal to the support function of the associated Wulff shape $\mathcal{W}$. We next comment on this point, first discussed by Dobrushin and Shlosman (1992) and Messager et al. (1992).

Let $A_0, \ldots, A_d \in \mathbf{R}^d$ be any set of $d+1$ points in general position and, for $i = 0, \ldots, d$, let Δ_i be the $(d-1)$-dimensional simplex defined by all these points except A_i. Denote by $|\Delta_i|$ the $(d-1)$-dimensional area of Δ_i and by $\mathbf{n}_i$ the unit vector orthogonal to Δ_i. The first vector, $\mathbf{n}_0$, is oriented toward the exterior of the simplex $A_0, \ldots, A_d$, while the others, $\mathbf{n}_i$, $i = 1, \ldots, d$, are oriented inside. We say that $\tau(\mathbf{n})$ satisfies the pyramidal inequality if

$$|\Delta_0|\, \tau(\mathbf{n}_0) \leq \sum_{i=1}^{d} |\Delta_i|\, \tau(\mathbf{n}_i) \tag{1.17}$$

for any set $A_0, \ldots, A_d$. We introduce the function on $\mathbf{R}^d$ defined by

$$f(\mathbf{x}) = |\mathbf{x}|\, \tau(\mathbf{x}/|\mathbf{x}|) \tag{1.18}$$

If this function is convex, it satisfies

$$f(\alpha \mathbf{x}) = \alpha f(\mathbf{x}) \tag{1.19}$$

$$f(\mathbf{x} + \mathbf{y}) \leq f(\mathbf{x}) + f(\mathbf{y}) \tag{1.20}$$

for any $\alpha > 0$ and any $\mathbf{x}$ and $\mathbf{y}$ in $\mathbf{R}^d$. The first condition, that $f(\mathbf{x})$ is a positively homogeneous convex function of degree 1, is clear from the definition. The second is equivalent in this case to the convexity condition.

Theorem 1.4. *The following propositions are equivalent*

1) $\tau(\mathbf{n})$ *satisfies the pyramidal inequality*

2) the function $f(\mathbf{x})$ *is convex*

3) $\tau(\mathbf{n})$ *is the support function of the convex body* $\mathcal{W}$

Proof. For simplicity we shall restrict ourselves to the three dimensional case. Assume that condition 3) is satisfied and let us consider the set $\mathcal{W}$ and its tangent planes orthogonal to $\mathbf{n}_0, \ldots, \mathbf{n}_3$. These planes form a pyramid whose four vertices are denoted by A_0, A_1, A_2, A_3. The notation is chosen in such a way that the plane A_1, A_2, A_3 separates the origin O from the vertex A_0. This is possible, for all such pyramids, if and only if $\mathcal{W}$ is convex. We consider also the four pyramids having as vertices the origin and three of these points. The volumes of these pyramids satisfy

$$|OA_1A_2A_3| \leq |OA_0A_2A_3| + |OA_0A_3A_1| + |OA_0A_1A_2| \tag{1.21}$$

Taking into account that the heights of these pyramids are $\tau(\mathbf{n}_0)$, $\tau(\mathbf{n}_1)$, $\tau(\mathbf{n}_2)$ and $\tau(\mathbf{n}_3)$, respectively, we get the pyramidal inequality for the pyramid A_0, A_1, A_2, A_3. This shows that conditions 1) and 3) are equivalent.

Next, we observe that

$$|\Delta_0|\,\mathbf{n}_0 = |\Delta_1|\,\mathbf{n}_1 + |\Delta_2|\,\mathbf{n}_2 + |\Delta_3|\,\mathbf{n}_3 \tag{1.22}$$

Thus the pyramidal inequality says that

$$f(\mathbf{x}_1 + \mathbf{x}_2 + \mathbf{x}_3) \leq f(\mathbf{x}_1) + f(\mathbf{x}_2) + f(\mathbf{x}_3) \tag{1.23}$$

with $\mathbf{x}_k = |\Delta_k|\,\mathbf{n}_k,\ k = 1, \ldots, 3$. Then, to prove (1.20), it is enough to find pyramids such that

$$|\Delta_1|\,\mathbf{n}_1 \to \mathbf{x}, \quad |\Delta_2|\,\mathbf{n}_2 \to \mathbf{y}, \quad |\Delta_3|\,\mathbf{n}_3 \to 0 \tag{1.24}$$

for all $\mathbf{x}$ and $\mathbf{y}$. This can easily be done and proves the equivalence of 1) and 2).

The pyramidal inequality may be interpreted as a thermodynamic stability condition and thus also the convexity of $f(\mathbf{x})$. If one supposes that $|\Delta_0|\,\tau(\mathbf{n}_0)$ is greater than the right hand side of inequality (1.17) this would make the interface bounded by the sides of Δ_0 unstable and difficult to realize.

Let us mention that the term of support function is usually attributed to the convex function $f(\mathbf{x})$. In fact a support function can be defined, by the same expression, for any convex set in $\mathbf{R}^d$, and it is a real (or $+\infty$) valued function, positively homogeneous and convex. For a non-empty convex body the convex function $f(\mathbf{x})$ is finite and hence (see e.g. Ruelle 1969, Proposition 3.3.4) Lipschitz continuous.

If $f(\mathbf{x}) = f(-\mathbf{x})$ the convex body $\mathcal{W}$ is symmetric with respect to the origin. Now, if $\mathcal{W}$ is a symmetric closed bounded convex set and the origin belongs to the interior of $\mathcal{W}$, then the support function of $\mathcal{W}$ is finite everywhere, symmetric and strictly positive except at the origin, i.e., it is a norm. Let then $\tilde{f}(\mathbf{x}) = \sup_{\mathbf{y}} \big(\mathbf{x} \cdot \mathbf{y}/f(\mathbf{y})\big)$ be the dual norm. In this case, the Wulff equilibrium shape $\mathcal{W}$ can be interpreted as the unit ball with respect to the dual norm

$$\mathcal{W} = \{\mathbf{x} \in \mathbf{R}^d : \tilde{f}(\mathbf{x}) \leq 1\} \tag{1.25}$$

1.4 Legendre transformation

The Wulff construction can also be viewed as a geometrical version of the Legendre transformation. We consider the function $f(\mathbf{x})$, defined from the surface tension $\tau(\mathbf{n})$ by equation (1.18), but we do not require now that f is the support function of a convex body. From definition (1.2), we get

$$\mathcal{W} = \{\mathbf{x} \in \mathbf{R}^d : f^*(\mathbf{x}) \leq 0\} \tag{1.26}$$

where f^* is the Legendre transform of f,

$$f^*(\mathbf{x}) = \sup_{\mathbf{y}} \big(\mathbf{x}\cdot\mathbf{y} - f(\mathbf{y})\big) \tag{1.27}$$

Actually $f^*(\mathbf{x}) = 0$ if $\mathbf{x} \in \mathcal{W}$, and $f^*(\mathbf{x}) = \infty$ otherwise. The support function of $\mathcal{W}$ is given by f^{**}, the Legendre transform of f^*.

This point of view was developed by Andreev (1981). For simplicity we consider the case $d = 3$ and assume also that $\mathcal{W}$ is symmetric with respect to the origin. We introduce a function φ on $\mathbf{R}^2$ such that the graph of $x_3 = \varphi(x_1, x_2)$, for $x_3 > 0$, coincides with the boundary $\partial\mathcal{W}$ of the crystal shape. Since $\mathcal{W}$ is a convex body, φ is a concave function, and

$$\mathcal{W} = \{\mathbf{x} \in \mathbf{R}^3 : -\varphi(-x_1, -x_2) \le x_3 \le \varphi(x_1, x_2)\} \tag{1.28}$$

In the present context this means that $-\varphi$ is the Legendre transform of the projected surface tension $\tau_p = (1/n_3)\tau$, considered as a function on $\mathbf{R}^2$ of the slopes $x_1 = n_1/n_3, x_2 = n_2/n_3$). In other words,

$$\tau_p(x_1, x_2) = f(x_1, x_2, 1) \tag{1.29}$$

Indeed, from equations (1.26) and (1.27), we see that

$$-\varphi(x_1, x_2) = \sup_{y_1, y_2} \big(x_1 y_1 + x_2 y_2 - \tau_p(y_1, y_2)\big) \tag{1.30}$$

Formula (1.28) is known as the Andreev construction. The interest of this approach comes from the fact that φ, and hence, the crystal shape itself, may be regarded as the free energy associated to a certain statistical mechanical Gibbs ensemble. We shall consider this ensemble in section 3.

1.5 Facets in the equilibrium crystal

Another consequence of the convexity properties, which will next be discussed (following Miracle-Sole 1995a), concerns the formation of facets in the equilibrium crystal. The facets of a crystal have certain particular orientations. Let $\mathbf{n}_0$ be the normal corresponding to one of these orientations, and denote by $\tau(\theta, \phi)$ the function $\tau(\mathbf{n})$ expressed in terms of the spherical co-ordinates, $0 \le \theta \le \pi$, $0 \le \phi \le 2\pi$, of $\mathbf{n}$, the vector $\mathbf{n}_0$ being taken as the polar axis.

Theorem 1.5. *Assume that the convexity condition is satisfied. A facet orthogonal to the direction $\mathbf{n}_0$ appears in the Wulff shape if, and only if, the derivative $\partial\tau(\theta, \phi)/\partial\theta$ is discontinuous at the point $\theta = 0$, for all ϕ. Moreover, the one-sided derivatives $\partial\tau(\theta, \phi)/\partial\theta$, at $\theta = 0^+$ and $\theta = 0^-$, exist, and determine the shape of the facet.*

Proof. In terms of the function f defined by (1.18), the Wulff shape $\mathcal{W}$ is the set of all $\mathbf{x} = (x_1, x_2, x_3) \in \mathbf{R}^3$ such that

$$x_1 y_1 + x_2 y_2 + x_3 y_3 \leq f(\mathbf{y}) \tag{1.31}$$

for every $\mathbf{y} \in \mathbf{R}^3$. If the coordinate axes are placed in such a way that $\mathbf{n}_0 = (0, 0, 1)$, the plane $x_3 = \tau(0)$ (where $\tau(0)$ is the value of τ for $\theta = 0$) is a tangent plane to $\mathcal{W}$. The facet $\mathcal{F}$ is the portion of this plane contained in $\mathcal{W}$. These facts follow from the convexity of f, which implies that f is the support function of $\mathcal{W}$. According to (1.31), the facet $\mathcal{F}$ consists of the points $(x_1, x_2, \tau(0)) \in \mathbf{R}^3$ such that

$$x_1 y_1 + x_2 y_2 \leq f(y_1, y_2, y_3) - y_3 \tau(0) = f(y_1, y_2, y_3) - y_3 f(0, 0, 1) \tag{1.32}$$

for all $\mathbf{y} = (y_1, y_2, y_3)$. Or, equivalently, such that

$$x_1 y_1 + x_2 y_2 \leq g(y_1, y_2) = \inf_{y_3} \ \big(f(y_1, y_2, y_3) - y_3 f(0, 0, 1) \big) \tag{1.33}$$

Restricting the infimum to $y_3 = 1/\lambda \geq 0$, and using the positive homogeneity and the convexity of f, one obtains

$$g(y_1, y_2) = \lim_{\lambda \to 0, \lambda \geq 0} (1/\lambda) \ \big(f(\lambda y_1, \lambda y_2, 1) - f(0, 0, 1) \big) \tag{1.34}$$

This implies that g is a positively homogeneous convex function on $\mathbf{R}^2$. Define

$$\mu(\phi) = g(\cos\phi, \sin\phi) \tag{1.35}$$

From (1.34), and taking $\lambda = \tan\theta$, one gets

$$\begin{aligned} \mu(\phi) &= \lim_{\theta \to 0, \theta \geq 0} (1/\sin\theta) \ \big(f(\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta) - \cos\theta f(0, 0, 1) \big) \\ &= \lim_{\theta \to 0, \theta \geq 0} (1/\theta) \ \big(\tau(\theta, \phi) - \tau(0) \big) = (\partial/\partial\theta)_{\theta = 0^+} \tau(\theta, \phi) \end{aligned} \tag{1.36}$$

Similarly

$$\mu(\phi + \pi) = g(-\cos\phi, -\sin\phi) = -(\partial/\partial\theta)_{\theta = 0^-} \tau(\theta, \phi) \tag{1.37}$$

Equations (1.33) and (1.35) show that both one-sided derivatives of exit and, from the convexity of g, it follows that

$$\mu(\phi + \pi) \leq \mu(\phi) \tag{1.38}$$

Thus, the hypothesis of the discontinuity of the derivative $\partial\tau/\partial\theta$, at $\theta = 0$, implies the strict inequality in (1.38) and shows that the convex set $\mathcal{F}$, given by (1.33), has a non-empty interior. This ends the proof of the Theorem.

Notice that, according to condition (1.33), the shape of the facet is given by

$$\mathcal{F} = \left\{ \mathbf{x} \in \mathbf{R}^2 : \mathbf{x} \cdot \mathbf{m} \leq \mu(\mathbf{m}) \right\} \tag{1.39}$$

where the inequality is assumed for every unit vector $\mathbf{m} = (\cos\phi, \sin\phi)$.

If $\tau(\theta, \phi) = \tau(\pi - \theta, \phi)$ the crystal shape is reflection symmetric with respect to the plane $x_3 = 0$. Then $\mu(\mathbf{m}) = \mu(-\mathbf{m})$ (assuming also the symmetry with respect to the origin), and the facet $\mathcal{F}$ has a center at the point $P_0 = (0, 0, \tau(0))$. This is not always the case, however, and the point P_0 can also be outside $\mathcal{F}$.

1.6 Crystal on a wall

The variational problem, considered in section 1.1, can be solved by purely geometrical means also in the presence of walls. We refer the reader the to paper by Kotecky and Pfister (1994) for a general analysis of these situations, and consider here, as a basic illustration, the case of a crystal on a single wall (Winterbottom 1967).

In this case, the surface tension of the boundary of the phase c in contact with the medium differs from that arising with the wall w. We suppose that the wall is described by a plane perpendicular to the unit vector $\mathbf{n}_0$, and that

$$E = \left\{ \mathbf{x} \in \mathbf{R}^d : \mathbf{x} \cdot \mathbf{n}_0 < a \right\} \tag{1.40}$$

is the half-space where we have the phases c and m. The surface tension between the phases c and m is denoted by $\tau(\mathbf{n})$. The relevant physical quantity in this problem is the difference

$$\sigma(\mathbf{n}_0) = \tau_{cw}(\mathbf{n}_0) - \tau_{mw}(\mathbf{n}_0) \tag{1.41}$$

where τ_{cw} and τ_{mw} are the surface free energies of the phase c with the wall and of the phase c with the wall, respectively. Since $\sigma(\mathbf{n}_0)$ is a difference of free energies, it may be positive or negative.

When $\sigma(\mathbf{n}_0) \geq \tau(\mathbf{n}_0)$ we have a drying situation: in equilibrium, it is preferable that the medium m occupies the place between the wall and the phase c, and consequently the phase c is not in contact with the wall. On the other hand, when $\sigma(\mathbf{n}_0) \leq -\tau(\mathbf{n}_0)$ we have a (complete) wetting situation: in equilibrium, the phase c forms a layer between the wall and the medium m.

In all other cases we speak of partial drying or partial wetting. Then, if B is the shape of the phase c, the total surface free energy is given by

$$\tau(\partial B) = |\partial B \cap \partial E|\, \sigma(\mathbf{n}_0) + \int_{\xi \in \partial B \cap E} \tau(\mathbf{n}(\xi)) ds_\xi \tag{1.42}$$

where the first term is the contribution of the boundary of the crystal along the wall and the second is the integral over the remaining part of the boundary of the crystal. The solution of the variational problem for the functional

(1.42) is the Winterbottom shape $\mathcal{W}$, and can be obtained as follows. One first constructs the Wulff shape $\mathcal{W}_\tau$ associated to the function $\tau(\mathbf{n})$ which corresponds to the ideal shape of the free crystal (formula (1.2)). Then we take the intersection of this set with the half space defined by the plane orthogonal to $\mathbf{n}_0$, at a distance $\sigma(\mathbf{n}_0)$ from the origin, i.e.,

$$\mathcal{W} = \mathcal{W}_\tau \cap \left\{ \mathbf{x} \in \mathbf{R}^d : \mathbf{x} \cdot \mathbf{n}_0 < \sigma(\mathbf{n}_0) \right\} \tag{1.43}$$

We notice that the set $\mathcal{W}$ is a convex body, still defined according to formula (1.2), but with the surface tension being replaced by $\sigma(\mathbf{n}_0)$ when $\mathbf{n}_0$ is the oriented normal to the interface. Thus, equation (1.43) follows, by arguing as in the proof of Theorem 1.1, from the isoperimetric inequality.

1.7 Stability of the Wulff solution

Let us finally comment on the stability of the Wulff shape as the solution to the variational problem of section 1.1. In the two-dimensional case, in addition to the isoperimetric inequality, the stability of the minimum in Theorem 1.1 can be controlled. The following classical inequality, known as the Bonnensen inequality, gives an estimate from below of the isoperimetric defect in the case of the circle. Suppose that a closed curve of length L bounds a plane domain B, of area F, and suppose that r and R are the radii of the incircle and the circumcircle, i.e., the largest circle contained in B and the smallest circle containing B. Then

$$L^2 - 4\pi F \geq \pi^2 (R^2 - r^2) \tag{1.44}$$

In the general case, when $\mathcal{W}$ is a convex body, a similar inequality for the isoperimetric defect

$$\tau_{\mathcal{W}}(\partial B)^2 - 4\,|\mathcal{W}|\,|B| \tag{1.45}$$

has been proved by Dobrushin et al. (1992).

There are no estimates of this kind in the three dimensional case. In two dimensions we have that if $\tau_{\mathcal{W}}(\partial B) - \tau_{\mathcal{W}}(\partial \mathcal{W})$ tends to zero, and $|B| = |\mathcal{W}|$, then the Hausdorff distance

$$\mathrm{dist}_H(\partial \mathcal{W}, B') = \max\{ \sup_{x \in \partial \mathcal{W}} \mathrm{dist}(x, \partial B),\ \sup_{x \in \partial B} \mathrm{dist}(x, \partial \mathcal{W}) \} \tag{1.46}$$

between the boundaries of $\mathcal{W}$ and of a suitably chosen translated B' of B, tends also to zero. This is true in three dimensions if both $\mathcal{W}$ and B are convex bodies, because of Diskant inequalities (see for instance Burago and Zalgaller 1988), and some appropriate distance could also be suggested between general $\mathcal{W}$ and B, in order to have the stability of the Wulff solution. However, the smallness of the difference $\tau_{\mathcal{W}}(\partial B) - \tau_{\mathcal{W}}(\partial \mathcal{W})$ does not imply anymore the smallness of the Hausdorff distance between $\partial B'$ and $\partial \mathcal{W}$. This is because a "hair" attached to the Wulff surface does not contribute

significantly to the total surface free energy. From the point of view of thermodynamics, the Wulff shapes with long hairs appear to have almost the same free energy as the equilibrium shape.

2 Interfaces in statistical mechanics

In this and the following sections we study some aspects of the theory of the coexistence of phases in statistical mechanics.

In the first approximation one can model the interatomic forces in a crystal by a lattice gas. These systems consist of lattice cells which may be either empty or occupied by a single particle. In a typical two-phase equilibrium state there is a dense component, which can be identified as the crystal phase, and a dilute phase, which can be identified as the vapor phase. The underlying lattice structure implies that the crystal phase is anisotropic, while this assumption, though unrealistic for the vapor phase, should be immaterial for the description of the crystal-vapor interface. As an illustrative example of such systems, the ferromagnetic Ising model will be considered.

The Ising model is defined on the d-dimensional cubic lattice $\mathcal{L} = \mathbf{Z}^d$, with configuration space $\Omega = \{-1, 1\}^{\mathcal{L}}$. The value $\sigma(i)$ is the spin at the site i. The occupation numbers $n(i) = (1/2)(\sigma(i) + 1$, which take the values 0 or 1, give the lattice gas version of this model. The energy of a configuration $\sigma_\Lambda = \{\sigma(i), i \in \Lambda\}$, in a finite box $\Lambda \subset \mathcal{L}$, under the boundary conditions $\bar{\sigma} \in \Omega$, is

$$H_\Lambda(\sigma_\Lambda \mid \bar{\sigma}) = - \sum_{\langle i,j\rangle \cap \Lambda \neq \emptyset} \sigma(i)\sigma(j) \tag{2.1}$$

where $\langle i, j\rangle$ are pairs of nearest neighbour sites and $\sigma(i) = \bar{\sigma}(i)$ if $i \notin \Lambda$. The partition function, at the inverse temperature $\beta = 1/kT$, is given by

$$Z^{\bar{\sigma}}(\Lambda) = \sum_{\sigma_\Lambda} \exp\big(- \beta H_\Lambda(\sigma_\Lambda \mid \bar{\sigma})\big) \tag{2.2}$$

The following limit, which is independent of the boundary conditions,

$$f(\beta) = \lim_{\Lambda \to \infty} -\frac{1}{\beta|\Lambda|} \ln\, Z^{\bar{\sigma}}(\Lambda) \tag{2.3}$$

defines the free energy per unit volume.

It is known that this model presents, at low temperatures $T < T_c$, where T_c is the critical temperature, two distinct thermodynamic pure phases, a positively and a negatively magnetized phase (or a dense and a dilute phase in the lattice gas language). This means two extremal translation invariant

Gibbs states, which correspond to the limits, when $\Lambda \to \infty$, of the finite volume Gibbs measures

$$Z^{\bar\sigma}(\Lambda)^{-1} \exp\big(- H_\Lambda(\sigma_\Lambda \mid \bar\sigma)\big) \tag{2.4}$$

with boundary conditions $\bar\sigma$ respectively equal to the ground configurations $(+)$ and $(-)$, such that $\bar\sigma(i) = 1$ and $\bar\sigma(i) = -1$, for all $i \in \mathcal{L}$. On the other side, if $T \geq T_c$, then the Gibbs state is unique (see, for instance, Ruelle 1969, Gallavotti 1972b, Miracle-Sole 1976).

Each configuration inside Λ can be geometrically described by specifying the set Peierls contours, which indicate the boundaries between the regions of spin 1 and the regions of spin -1. Unit square surfaces are placed midway between nearest-neighbour pairs of sites i and j, and perpendicular to these bonds, if $\sigma(i)\sigma(j) = -1$. The connected components of this set are the Peierls contours. Under the above boundary conditions $(+)$ and $(-)$, they form a set of closed polyhedrical surfaces. The contours can be viewed as defects, or excitations, with respect to the ground states of the system (the constant configurations 1 and -1), and are a basic tool for the investigation of the model at low temperatures.

2.1 The surface tension

In order to study the interface between the two pure phases one needs to construct a state describing the coexistence of these phases. Let Λ be a parallelepiped of sides $L_1, \ldots, L_d$, parallel to the axes, and centered at the origin of $\mathcal{L}$, and let $\mathbf{n} = (n_1, \ldots, n_d)$ be a unit vector in $\mathbf{R}^d$, such that $n_d \neq 0$. Introduce the mixed boundary conditions $(\pm, \mathbf{n})$, for which $\bar\sigma(i) = 1$ if $i \cdot \mathbf{n} \geq 0$, and $\bar\sigma(i) = -1$ if $i \cdot \mathbf{n} < 0$. These boundary conditions force the system to produce a defect going transversely through the box Λ, a big Peierls contour that can be interpreted as a microscopic interface. The other defects that appear above and below the interface can be described by closed contours inside the pure phases.

The free energy, per unit area, due to the presence of the interface, is the surface tension. It can be defined by

$$\tau(\mathbf{n}) = \lim_{L_1,\ldots,L_{d-1}\to\infty} \lim_{L_d\to\infty} -\frac{n_d}{\beta L_1 \ldots L_{d-1}} \ln \frac{Z^{(\pm,\mathbf{n})}(\Lambda)}{Z^{(+)}(\Lambda)} \tag{2.5}$$

Notice that in this expression the volume contributions proportional to the free energy of the coexisting phases, as well as the boundary effects, cancel, and only the contributions to the free energy of the interface are left.

Theorem 2.1 *The thermodynamic limit $\tau(\mathbf{n})$, of the interfacial free energy per unit area, exists, and is a non negative bounded function of $\mathbf{n}$. Its extension by positive homogeneity, $f(\mathbf{x}) = |\mathbf{x}|\,\tau(\mathbf{x}/|\mathbf{x}|)$, is a convex function on $\mathbf{R}^d$.*

A proof of these statements has been given by Messager et al. (1992) using correlation inequalities (this being the reason for their validity for all β). In fact the validity of this Theorem has been proved for a large class of lattice systems.

Moreover, for the Ising model we know, from Bricmont et al. (1980), Lebowitz and Pfister (1981) and the convexity condition, that $\tau(\mathbf{n})$ is strictly positive for $T < T_c$ and that it vanishes if $T \geq T_c$.

2.2 Interfaces at low temperatures

In Appendix A we give a résumé of the theory of cluster expansions. We are going to apply this theory to study the low temperature properties of the system. Let us first describe the cluster theory of a pure phase. We have seen above that a configuration in the box Λ, with $(+)$ boundary conditions, is characterized as a set $X = \{\gamma_1, \ldots, \gamma_n\}$ of closed mutually disjoint contours. It is easy to see that, up to a constant, the energy of the configuration is equal to twice the total area of the contours. Besides the mutual exclusion there is no other interaction between the contours. If to each contour we attribute the weight $\phi(\gamma) = \exp(-2\beta|\gamma|)$, where $|\gamma|$ is the area of the contour γ, we get, for the partition function $Z^{(+)}(\Lambda)$, an expression like equation (A.1), in Appendix A. The system can be viewed in terms of contours as a system of polymers, with weight $\phi(\gamma)$, and the convention that two contours are compatible if they do not intersect.

Let us next consider the convergence condition, Theorem A.2 in Appendix A. We introduce $\mu(\gamma) = \exp(-b|\gamma|)$ and remark that the number of contours cutting a given lattice bond and of area $|\gamma| = n$ is bounded by K^n, where K is certain constant (one can take $K = 3$ using appropriate definitions). Then, we have

$$\sum_{\gamma' \not\sim \gamma} \mu(\gamma') \leq |\gamma| \sum_n K^n e^{-bn} \leq |\gamma|(1 - Ke^{-b})^{-1} \tag{2.6}$$

This shows that the convergence condition (A.6) is satisfied if the temperature is sufficiently low, i.e., there exist a constant β_0 such that (A.6) is satisfied if $\beta \geq \beta_0$. Using formula (A.4) and estimate (A.7), one can then derive a convergent series expansion for the free energy of the system. Also, from (A.4) and (A.7), it follows that

$$Z^{(\pm,\mathbf{n})}(\Lambda)/Z^{(+)}(\Lambda) = \sum_{\mathcal{I}} e^{-2\beta|\mathcal{I}|} \exp\Big(- \sum_{X \cap \mathcal{I} \neq \emptyset} a^{\mathrm{T}}(X) \phi^X \Big) \tag{2.7}$$

where the first sum runs over all microscopic interfaces $\mathcal{I}$, compatible with the boundary conditions. The sum in the exponential runs over all clusters of contours that intersect $\mathcal{I}$. Each term in the first sum gives a weight proportional to the probability of the microscopic interface. From this, a

representation of the microscopic interface itself as a polymer system, can be derived.

Consider now the three-dimensional Ising model with the $(\pm, \mathbf{n}_0)$ boundary conditions, associated to the direction $\mathbf{n}_0 = (0, 0, 1)$, which define inside the box Λ a horizontal interface. At low temperatures $T > 0$, we expect the microscopic interface corresponding to these boundary conditions, which at $T = 0$ coincides with the plane $i_3 = -1/2$, to be modified by small deformations. The microscopic interface can then be described by means of its defects, or excitations, with respect to the interface at $T = 0$. These defects, called walls, form the boundaries (which may have some width), between the smooth plane portions of the interface. In this way the interface structure, with its probability distribution defined by equation (2.7), may be interpreted as a "gas of walls" on a two-dimensional lattice. There is an interaction between the walls, coming from the fact that the interface is surrounded by the $(+)$ phase from above and the $(-)$ phase from below. But the exponential function in equation (2.7), gives a mathematical description of this interaction in terms of clusters of contours. This allows us to define a "gas of aggregates of walls and clusters" as a polymers system on the two-dimensional lattice (see the original articles quoted below and, for instance, Miracle-Sole 1995a, Appendix, for a short review).

Dobrushin (1972) proved the dilute character of this gas at low temperatures, which means that the interface is essentially flat (or rigid). The considered boundary conditions yield indeed a non translation invariant Gibbs state. Furthermore, cluster expansion techniques have been applied by Bricmont et al. (1979), to study the interface structure in this case (see also Holicky et al. 1988).

The same analysis applied to the two-dimensional model shows a different behavior at low temperatures. In this case the walls belong to a one-dimensional lattice, and Gallavotti (1972) proved that the microscopic interface undergoes large fluctuations of order $\sqrt{L_1}$. The interface does not survive in the thermodynamic limit, $\Lambda \to \infty$, and the corresponding Gibbs state is translation invariant. Moreover, the interface structure can be studied by means of a cluster expansion for any orientation of the interface (see also Bricmont et al. 1981).

In the three-dimensional case, the description of the microscopic interface for any orientation $\mathbf{n}$, leads to very difficult problems of random surfaces. It is possible, however, by introducing a new polymer system, to analyze also the interfaces which are near to the particular orientations $\mathbf{n}_0$, discussed above. This problem, related to the formation of facets in the equilibrium crystal, will be treated in section 4.

3 On the microscopic proof of the Wulff construction

In this section we consider a simplified model of the two dimensional interface. We represent the interface as a single-valued function over a reference line. At each site i of the lattice $\mathbf{Z}$ an integer variable h_i is assigned which indicates the height of the interface at this site. One obtains a statistical mechanical model by assigning an energy to each configuration $\mathbf{h} = \{h_0, h_1, ..., h_N\}$, in the box $0 \leq i \leq N$, of length N. The standard example is

$$H_N(\mathbf{h}) = \sum_{i=1}^{N} (1 + |h_i - h_{i-1}|) \tag{3.1}$$

which corresponds to the solid-on-solid (SOS) model. Then the energy of a configuration coincides with the length of the interface. The weight of a given configuration, at the inverse temperature β, is proportional to the Boltzmann factor $\exp\big(-\beta H_\Lambda(\phi)\big)$. Provided that the energy remains unchanged under the global shift h_i to $h_i + b$, for all i and all $b \in \mathbf{Z}$, there is considerable freedom of how to choose the energy function. The results below apply, also, to more general Hamiltonians of this form.

The model provides an approximate description of an interface separating two phases at equilibrium, such as the positively and negatively magnetized phases of the three-dimensional Ising model. Actually the SOS model may be obtained as the limit of the anisotropic Ising model, when we let the coupling constant, in the vertical direction, tend to infinity.

We are going to study the statistical mechanics of the SOS model, with the global constraint of having a specified area between the interface and the horizontal axis, and to show the existence of the thermodynamic limits and the equivalence of the Gibbs ensembles associated with this problem. As a corollary, it can be seen that the configurations of a large system follow a well defined mean profile with probability one, the shape of the phase boundary at equilibrium. This gives a simple alternative microscopic proof of the validity of the Wulff construction for such models, first established by DeConink, et al. (1989). The fluctuations of the interface around the mean profile have recently been studied by Dobrushin and Hryniv (1996) following the same approach.

3.1 Surface tension and Wulff shape

We introduce first the Gibbs ensemble which consists of all configurations, in the box of length N, with specified boundary conditions $h_0 = 0$ and $h_N = Y$. The associated partition function is given by

$$Z_1(N, Y) = \sum_{\mathbf{h}} e^{-\beta H(\mathbf{h})}\ \delta(h_0)\delta(h_N - Y) \tag{3.2}$$

where the sum runs over all configurations in the box and $\delta(t)$ is the discrete Dirac delta ($\delta(t) = 1$ if $t = 0$ and $\delta(t) = 0$ otherwise). We define the corresponding free energy per site as the limit

$$\tau_p(y) = \lim_{N\to\infty} -\frac{1}{\beta N} \ln Z_1(N, yN) \tag{3.3}$$

where $y = -\tan\theta$, the slope of the interface, is a real number. This free energy is called the projected surface tension. The surface tension, which represents the interfacial free energy per unit length of the mean interface, is

$$\tau(\theta) = \cos\theta \; \tau_p(-\tan\theta) \tag{3.4}$$

We introduce a second Gibbs ensemble, conjugate to the previous ensemble, whose partition function, in the box of length N, is given by

$$Z_2(N, x) = \sum_{\mathbf{h}} e^{-\beta H(\mathbf{h})} e^{\beta x h_N} \; \delta(h_0) \tag{3.5}$$

where $x \in \mathbf{R}$, replaces as a thermodynamic parameter the slope y. We define the associated free energy as

$$\varphi(x) = \lim_{N\to\infty} -\frac{1}{\beta N} \ln Z_2(N, x) \tag{3.6}$$

Theorem 3.1. *Limits (3.3) and (3.6), which define the above free energies, exist. The first, τ_p, is a convex even function of y. The second, φ, is a concave even function of x. Moreover, τ_p and $-\varphi$ are conjugate convex functions, i.e., they are related by the Legendre transformations*

$$\begin{aligned} -\varphi(x) &= \sup_y \; \big(xy - \tau_p(y)\big) \\ \tau_p(y) &= \sup_x \; \big(xy + \varphi(x)\big) \end{aligned} \tag{3.7}$$

The validity of the above statements follows from the subadditivlty property

$$\ln Z_1(N_1 + N_2, y(N_1 + N_2)) \geq \ln Z_1(N_1, yN_1) + \ln Z_1(N_2, yN_2) \tag{3.8}$$

which is straightforward, and standard arguments in the theory of the thermodynamic limit (Ruelle 1969, Galgani et al. 1971). See also, for instance, Messager et al. (1992) for a proof of these statements in a more general setting.

The convexity of τ_p is equivalent to the fact that the surface tension τ satisfies the pyramidal inequality (see section 1.3). Relations (3.7) between

the free energies express the thermodynamic equivalence of the two ensembles (3.2) and (3.5). These relations imply that the curve $z = \varphi(x)$ gives, according to the Wulff construction, or the equivalent Andreev construction, the equilibrium shape of the crystal associated to our system (see section 1.4).

The function $\varphi(x)$ defined by (3.6) is easily computed by summing a geometrical series. One introduces the difference variables

$$n_i = h_{i-1} - h_i \tag{3.9}$$

for $i = 1, ..., N$, so that the partition function factorizes and one obtains

$$\varphi(x) = 1 - \beta^{-1} \ln \sum_n e^{-\beta|n| + \beta x n} \tag{3.10}$$

The explicit form of this function is

$$\varphi(x) = 1 - \beta^{-1} \ln \frac{\sinh \beta}{\cosh \beta - \cosh \beta x} \tag{3.11}$$

if $-1 < x < 1$, and $\varphi(x) = -\infty$ otherwise.

3.2 The volume constraint

We next define two new Gibbs ensembles. In the first of these ensembles we consider the configurations such that $h_N = 0$, which have a specified height at the origin $h_0 = M$ and which have a specified volume (area) V between the interface and the horizontal axis, this volume being counted negatively for negative heights,

$$V = V(\mathbf{h}) = \sum_{i=0}^{N} h_i \tag{3.12}$$

The corresponding partition function is

$$Z_3(N, V, M) = \sum_{\mathbf{h}} e^{-\beta H(\mathbf{h})} \ \delta(h_N) \delta(V(\mathbf{h}) - V) \delta(h_0 - M) \tag{3.13}$$

where V and M are understood as their integer parts when they do not belong to $\mathbf{Z}$. The second ensemble is the conjugate ensemble of (3.13). Its partition function is given by

$$Z_4(N, u, \mu) = \sum_{\mathbf{h}} e^{-\beta H(\mathbf{h})} \ e^{\beta u (V(\mathbf{h})/N) + \beta \mu h_0} \ \delta(h_N) \tag{3.14}$$

where $u \in \mathbf{R}$ and $\mu \in \mathbf{R}$ are the conjugate variables. Our next step will be to prove the existence of the thermodynamic limit for these ensembles and their equivalence in this limit.

Theorem 3.2. *The following limits exist*

$$\psi_3(v,m) = \lim_{N\to\infty} -\frac{1}{\beta N}\ \ln Z_3(N, vN^2, mN) \tag{3.15}$$

$$\psi_4(u,\mu) = \lim_{N\to\infty} -\frac{1}{\beta N}\ \ln Z_4(N, u, \mu) \tag{3.16}$$

and define the free energies per site associated to the considered ensembles. Moreover, ψ_3 and $-\psi_4$ are conjugate convex functions

$$\begin{aligned} -\psi_4(u,\mu) &= \sup_{v,m}\ \big(uv + \mu m - \psi_3(v,m)\big) \\ \psi_3(v,m) &= \sup_{u,\mu}\ \big(uv + \mu m + \psi_4(u,\mu)\big) \end{aligned} \tag{3.17}$$

The crucial observation for proving this Theorem is the subadditivity property given below. Then we adapt known arguments (Ruelle 1969, Galgani et al. 1971) in the theory of the thermodynamic limit. For a more detailed proof see Miracle-Sole and Ruiz (1994) or Dobrushin and Hryniv (1996).

Proposition. The partition function Z_3 satisfies the subadditivity property

$$\begin{aligned} &Z_3(2N, 2(V'+V''), M'+M'') \geq \\ &\qquad Z_3(N, V', M')\ Z_3(N, V'', M'')\ e^{-2\beta|M''|/(2N-1)} \end{aligned} \tag{3.18}$$

Proof. In order to prove this property we associate a configuration $\mathbf{h}$ of the first system in the box of length $2N$, to a pair of configurations $\mathbf{h}'$ and $\mathbf{h}''$ of the system in a box of length N, as follows

$$\begin{aligned} h_{2i} &= h'_i + h''_i\ , i = 0, \dots, N \\ h_{2i-1} &= h'_{i-1} + h''_i\ , i = 1, \dots, N \end{aligned} \tag{3.19}$$

Then $h_{2N} = h'_N + h''_N = 0$, $h_0 = h'_0 + h''_0 = M' + M''$ and

$$\begin{aligned} V(\mathbf{h}) &= 2\sum_{i=1}^{N} h'_i + \sum_{i=0}^{N} h''_i + \sum_{i=1}^{N} h''_i \\ &= 2\ \big(V(\mathbf{h}') + V(\mathbf{h}'')\big) - M'' \end{aligned} \tag{3.20}$$

This shows that the configuration $\mathbf{h}$ belongs to the partition function in the right hand side of (3.18). Since

$$H_{2N}(\mathbf{h}) = H_N(\mathbf{h}') + H_N(\mathbf{h}'') \tag{3.21}$$

because $n_{2i} = n'_i$ and $n_{2i-1} = n''_i$, as follows from (3.19), we get

$$Z_3(N, V', M')\ Z_3(N, V'', M'') \leq Z_3(2N, 2(V'+V'')-M'', M'+M'') \quad (3.22)$$

Then we use the change of variables

$$\begin{aligned} &\tilde{h}_i = h_i + (M''/(2N-1)),\ i = 1, \dots, 2N-1, \\ &\tilde{h}_0 = h_0,\ \tilde{h}_{2N} = h_{2N} = 0 \end{aligned} \quad (3.23)$$

which gives

$$Z_3(2N, V - M'', M) \leq e^{2\beta|M''|/(2N-1)}\ Z_3(2N, V, M) \quad (3.24)$$

to conclude the proof.

3.3 The Wulff construction

The free energies ψ_3 and ψ_4, associated to the system with the volume constraint, can be expressed in terms of the functions φ and τ_p introduced in section 3.2. We consider first the function ψ_4. In terms of the difference variables (3.9), we have

$$V(\mathbf{h}) = \sum_{i=0}^{N} h_i = \sum_{i=1}^{N}\ in_i \quad (3.25)$$

and, therefore,

$$Z_4(N, u, \mu) = \prod_{i=1}^{N} \Big(\sum_{n_i} e^{-\beta|n_i| + \beta(u/N)in_i + \beta\mu n_i} \Big) \quad (3.26)$$

Taking expression (3.10) into account it follows

$$Z_4(N, u, \mu) = \exp\Big(-\beta \sum_{i=1}^{N} \varphi\big(\frac{u}{N}i + \mu\big) \Big) \quad (3.27)$$

and

$$\psi_4(u, \mu) = \lim_{N\to\infty} \frac{1}{N} \sum_{i=1}^{N} \varphi\big(\frac{u}{N}i + \mu\big) = \lim_{N\to\infty} \frac{1}{u} \sum_{i=1}^{N} \frac{u}{N} \varphi\big(\frac{u}{N}i + \mu\big) \quad (3.28)$$

which, writing the Riemann sum as an integral, implies

$$\psi_4(u, \mu) = \frac{1}{u} \int_0^u \varphi(x + \mu) dx \quad (3.29)$$

Next we consider the free energy ψ_3. This function is determined by the Legendre transform (3.17). The supremum over u, μ is obtained for the values u_0, μ_0, for which the partial derivatives of the right hand side of equation (3.17) are zero:

$$\begin{aligned} v + (\partial\psi_4/\partial u)(u_0, \mu_0) &= 0 \\ m + (\partial\psi_4/\partial\mu)(u_0, \mu_0) &= 0 \end{aligned} \tag{3.30}$$

That is, for u_0, μ_0 which satisfy

$$\frac{1}{u_0^2}\int_0^{u_0} \varphi(x+\mu_0)dx - \frac{1}{u_0}\varphi(\mu_0+u_0) = v \tag{3.31}$$

$$\frac{1}{u_0}\big(\varphi(\mu_0) - \varphi(\mu_0+u_0)\big) = m \tag{3.32}$$

Then, from (3.17), (3.28), (3.31) and (3.32), we get

$$\psi_3(v,m) = 2\psi_4(u_0,\mu_0) - \frac{1}{u_0}\big((\mu_0+u_0)\varphi(\mu_0+u_0) - \mu_0\varphi(\mu_0)\big) \tag{3.33}$$

But, using relation (3.7) under the form

$$\varphi(x) = x\varphi'(x) + \tau_p(\varphi'(x)) \tag{3.34}$$

in (3.29) and integrating by parts, we get

$$2\psi_4(u_0,\mu_0) = \frac{1}{u_0}\int_{\mu_0}^{\mu_0+u_0} \tau_p(\varphi'(x))dx + \frac{1}{u_0}\big((\mu_0+u_0)\varphi(\mu_0+u_0) - \mu_0\varphi(\mu_0)\big) \tag{3.35}$$

Finally, this equation together with (3.33), implies

$$\psi_3(v,m) = \frac{1}{u_0}\int_{\mu_0}^{\mu_0+u_0} \tau_p(\varphi'(x))dx \tag{3.36}$$

To interpret these relations, let us consider the graph of the function $z = \phi(x)$ and an arc BC of this curve between the points B and C having the abcises μ_0 and $\mu_0 + u_0$, respectively. We draw the vertical line $x = \mu_0$ passing through the point B, and the horizontal line $z = \phi(\mu_0 + u_0)$ passing through the point C. Let A be the point where these two lines intersect. We observe that the right hand side of (3.31) represents the area ABC divided by $\overline{AC}^2$. Therefore, the values u_0, μ_0, which solve (3.31) and (3.32), are obtained when this area is equal to v, with the condition coming from (3.32), that the slope $\overline{AB}/\overline{AC}$, is equal to m. Then, according to (3.36), the free energy $\psi_3(v,m)$ is equal to the integral of the surface tension along the arc BC, of the curve $z = \varphi(x)$, divided by the same scaling factor $\overline{AC} = u_0$.

We conclude that, for large N, the configurations of the SOS model, with a prescribed area vN^2, follow a well defined mean profile, that is, the macroscopic profile given by the Wulff construction, with very small fluctuations. This follows from the fact that the probability of the configurations which deviate macroscopically from the mean profile is zero in the thermodynamic limit. The free energy associated to the configurations which satisfy the conditions above, and moreover, are constrained to pass through a given point not belonging to the mean profile, can be computed with the help of equation (3.13). Indeed, if the coordinates of the point are (x_1, m_1), then the partition function associated to such set of configurations is given by the product

$$Z_3\big(x_1N, V', (m-m_1)N\big)\ Z_3\big((1-x_1)N, V'', (m-m_1)N\big) \tag{3.37}$$

with moreover the condition $V' + V'' = vN^2$. As a consequence of equations (3.15) and (3.36), and knowing from the macroscopic variational problem that the arc BC is the shape which minimizes the integral of τ_p, we see that the probability of this set of configurations tends exponentially to zero as $N \to \infty$.

3.4 Remark

The mathematically rigorous justification of the Wulff construction, in the case of the two-dimensional Ising model at low temperatures, is due to Dobrushin et al. (1992, see also Dobrushin et al. 1993, for the statement of the main result and some ideas of the proof, and Pfister 1991, for another version of the same proof). Their results show that, in the canonical ensemble, where the total number of particles (or the total magnetization in the language of spin systems) is fixed, a (unique) droplet of the dense phase, immersed in the dilute phase, is formed. Its shape, when properly rescaled, obeys the Wulff principle. Ioffe (1994, 1995) extended these results, in the case of the two-dimensional Ising model, to all temperatures below the critical temperature.

4 Roughening transition and equilibrium shapes

Let us come back to the three-dimensional Ising model. We already know, from section 2, that the interface orthogonal to a lattice axis is rigid at low temperatures, and that the corresponding boundary conditions give rise to a non translation invariant Gibbs state. It is believed, that at higher temperatures, but before reaching the critical temperature T_c, the fluctuations of this interface become unbounded when the volume tends to infinity, so that the corresponding Gibbs state in the thermodynamic limit is translation invariant. The interface undergoes a roughening phase transition at a temperature $T = T_R < T_c$.

Recalling that the rigid interface may be viewed as a two-dimensional polymer system (the system of walls), one might expect that the critical temperature $T_c^{d=2}$, of the two-dimensional Ising model, is relevant for the roughening transition, and that T_R is somewhere near $T_c^{d=2}$. Indeed, approximate methods, used by Weeks et al. (1973), suggest $T_R \sim 0.53\ T_c$, a temperature slightly higher then $T_c^{d=2}$. Moreover, van Beijeren (1975) proved, using correlation inequalities, that $T_R \geq T_c^{d=2}$.

Since then, however, it appears to be no proof of the fact that $T_R < T_c$, i. e., that the roughening transition for the three-dimensional Ising model really occurs.

At present one is able to study rigorously the roughening transition only for some simplified models of the microscopic interface. Thus, Fröhlich and Spencer (1981) have proved this transition for the SOS (solid-on-solid) model. Moreover, several restricted SOS models, in which the differences of heights at two nearest neighbor sites are restrict to take a few number of values, are exactly solvable. They present also a roughening transition (this theory has been reviewed by Abraham 1986 and van Beijeren and Nolden 1987).

From a macroscopic point of view, the roughness of an interface should be apparent when considering the shape of the equilibrium crystal associated with the system. One knows that a typical equilibrium crystal at low temperatures has smooth plane facets linked by rounded edges and corners. The area of a particular facet decreases as the temperature is raised and the facet finally disappears at a temperature characteristic of its orientation. The reader will find information and references on equilibrium crystals in the review articles by Abraham (1986), van Beijeren and Nolden (1987), Kotecky (1989) and Rottman and Wortis (1984).

It can be argued that the roughening transition corresponds to the disappearance of the facet whose orientation is the same as that of the considered interface. The exactly solvable SOS models mentioned above, for which the function $\tau(\mathbf{n})$ has been computed, are interesting examples of this behavior (this subject has been reviewed by Abraham 1986, Chapter VII, see also Kotecky and Miracle-Sole 1986, 1987a, 1987b). This point will be briefly discussed in the next two sections, where several results on this subject, concerning the three-dimensional Ising model, will be reported. See Miracle-Sole (1995a) for the proofs and a more detailed discussion.

4.1 The step free energy

The step free energy plays an important role in the problem under consideration. It is defined, using appropriate boundary conditions, as the free energy associated with the introduction of a step of height 1 on the interface. This quantity can be regarded as an order parameter for the roughening transition, analogous, in some sense, to the surface tension in the case of the usual phase transitions. Indeed, Bricmont et al. (1982) proved that $\tau^{\text{step}} > 0$ if $T < T_c^{d=2}$, a result analogous to the above mentioned result by van Bei-

jeren (1975). On the other hand $\tau^{\rm step} = 0$ if $T \geq T_c$ (see, again, Bricmont et al. 1982).

In order to define the step free energy we consider a parallelepipedic box Λ, defined as in section 2 above, and introduce the (step, $\mathbf{m}$) boundary conditions, associated to the unit vectors $\mathbf{m} = (\cos\phi, \sin\phi) \in \mathbf{R}^2$, by

$$\bar\sigma(i) = \begin{cases} 1 & \text{if } i > 0 \text{ or if } i_3 = 0 \text{ and } i_1 m_1 + i_2 m_2 \geq 0 \\ -1 & \text{otherwise} \end{cases} \tag{4.1}$$

Then, the step free energy, for a step orthogonal to $\mathbf{m}$ (such that $m_2 \neq 0$), is

$$\tau^{\rm step}(\phi) = \lim_{L_1\to\infty} \lim_{L_2\to\infty} \lim_{L_3\to\infty} -\frac{\cos\phi}{\beta L_1} \ \ln \ \frac{Z^{(\rm step,\mathbf{m})}(\Lambda)}{Z^{(\pm,\mathbf{n}_0)}(\Lambda)} \tag{4.2}$$

Clearly, this expression represents the residual free energy due to the considered step, per unit length.

When considering the configurations under the (step, $\mathbf{m}$) boundary conditions, the step may be viewed as a defect on the rigid interface described in section 2. It is, in fact, a long wall going from one side to the other side of the box Λ. A more careful description of it can be obtained as follows. At $T = 0$, the step parallel to the axis (i. e., for $\mathbf{m} = (0, 1)$) is a perfectly straight step of height 1. At a low temperature $T > 0$, some deformations appear, connected by straight portions of height 1. The step structure, with its probability distribution in the corresponding Gibbs state, can then be described as a "gas" of these defects (to be called step-jumps). This system can be represented as a polymer system on a one-dimensional lattice. This description, somehow similar to the description of the interface of the two-dimensional Ising model used by Gallavotti (1972), is valid, in fact, for any orientation $\mathbf{m}$ of the step. It can be shown that the system of step-jumps, at low temperatures, satisfies the properties which are required for applying the cluster expansion techniques. In this way, the step structure can be studied. Actually, the step-jumps are not independent since the rest of the system produces an effective interaction between them. Nevertheless, this interaction can be treated by means of the low temperature expansion, in terms of walls, for the rigid interface, applied to the regions of the interface lying at both sides of the step. From this analysis (Miracle-Sole 1995a) one gets the following result.

Theorem 4.1. *If the temperature is low enough (i.e., if $T \leq T_0$, where $T_0 > 0$ is a given constant), then the step free energy $\tau^{\rm step}(\mathbf{m})$, exists in the thermodynamic limit, and extends by positive homogeneity to a strictly convex function. Moreover, $\tau^{\rm step}(\mathbf{m})$ can be expressed in terms of an analytic function of T, which can be obtained by means of a convergent cluster expansion.*

In fact,

$$\begin{aligned} \tau^{\rm step}(\mathbf{m}) = \ & 2(|m_1| + |m_2|) - (1/\beta)\big((|m_1| + |m_2|)\ln(|m_1| + |m_2|) \\ & - |m_1|\ln|m_1| - |m_2|\ln|m_2|\big) - (1/\beta)\varphi_{\mathbf{m}}(\beta) \end{aligned} \tag{4.3}$$

where $\varphi_{\mathbf{m}}$ is an analytic function of $z = e^{-2\beta}$, for $|z| \leq e^{-2\beta_0}$. The first two terms in this expression, which represent the main contributions for $T \to 0$, come from the ground state of the system under the considered boundary conditions. The first term can be recognized as the residual energy of the step at zero temperature and, the second term, as $-(1/\beta)$ times the entropy of this ground state. The same two terms occur in the surface tension of the two-dimensional Ising model (see Avron et al. 1982 and Dobrushin et al. 1992). By considering the lowest energy excitations, it can be seen that $\varphi_{\mathbf{m}}$ is $O(e^{-4\beta})$, and also, that the first term in which this series differs from the series associated to the surface tension of the two-dimensional Ising model, is $O(e^{-12\beta})$.

4.2 The shape of a facet

We have seen, in section 1.5, that the appearance of a facet in the equilibrium crystal shape is related, according to the Wulff construction, to the existence of a discontinuity in the derivative of the surface tension with respect to the orientation. In the case of the three-dimensional Ising model, a first result concerning this point, was obtained by Bricmont et al. (1986). These authors proved a correlation inequality which establish τ^{step} as a lower bound to the one-sided derivative $\partial\tau(\theta)/\partial\theta$ at $\theta = 0^+$ (here $\tau^{\text{step}} = \tau^{\text{step}}(0,1)$ and $\tau(\theta) = \tau(0, \sin\theta, \cos\theta)$). Thus $\tau^{\text{step}} > 0$ implies a kink in $\tau(\theta)$ at $\theta = 0$ and, therefore, a facet is expected.

In fact, τ^{step} should be equal to this one-sided derivative. This is reasonable, since the increment in surface tension of an interface tilted by an angle θ, with respect to the surface tension of the rigid interface, can be approximately identified, for θ small, with the free energy of a collection of steps. The density of the steps being proportional to θ, the distance between them becomes very large when θ is very small. But, if the interaction between the steps can be neglected, the free energy of the whole collection of steps can be approximated by the sum of the individual free energies of the steps.

With the help of the methods described in section 4.1, it is possible to study these free energies and to control the approximations involved in the problem. The following result can then be derived (see Miracle-Sole 1995a for the proof).

Theorem 4.2. *For $T < T_0$, we have*

$$\partial\tau(\theta,\phi)/\partial\theta|_{\theta=0^+} = \tau^{\text{step}}(\phi) \tag{4.4}$$

i. e., the step free energy equals the one-sided angular derivative of the surface tension.

It is natural to expect that this equality is true for any T less than T_R, and that for $T \geq T_R$, both sides in the equality vanish, and thus, the disappearance of the facet is involved. However, the condition that the temperature is low enough is important here. Only when it is fulfilled we have the full control on the equilibrium probabilities that is needed in the proofs.

The above relation, together with Theorem 1.5, implies that the shape of the facet is given by the two-dimensional Wulff construction applied to the step free energy $\tau^{\rm step}(\mathbf{m})$. Namely,

$$\mathcal{F} = \left\{\mathbf{x} \in \mathbf{R}^2 : \mathbf{x} \cdot \mathbf{m} \leq \tau^{\rm step}(\mathbf{m})\right\} \tag{4.5}$$

where the inequality is assumed for every unit vector $\mathbf{m}$ in $\mathbf{R}^2$. Then, from the properties of $\tau^{\rm step}$ mentioned above, it follows that the facet has a smooth boundary without straight segments and, therefore, that the crystal shape presents rounded edges and corners.

Appendix A : Cluster expansions

Let $\mathcal{P}$ be a countable or a finite set, the elements of which will be called polymers. Let $\mathcal{I} \subset \mathcal{P} \times \mathcal{P}$ be a reflexive and symmetric relation. We say that the elements $\gamma_1, \gamma_2 \in \mathcal{P}$ are incompatible if $(\gamma_1, \gamma_2) \in \mathcal{I}$, and we will also write $\gamma_1 \not\sim \gamma_2$. If $(\gamma_1, \gamma_2) \notin \mathcal{I}$ we say that the two polymers are compatible.

For each finite set $X \subset \mathcal{P}$, we define $a(X)$ to be 1 if any two distinct polymers $\gamma_1, \gamma_2 \in X$ are compatible, and 0 if some distinct $\gamma_1, \gamma_2 \in X$ has $\gamma_1 \not\sim \gamma_2$. We assume that a complex valued function $\phi(\gamma)$, $\gamma \in \mathcal{P}$ is given, and call $\phi(\gamma)$ the weight (or activity) of the polymer γ.

Let a finite set $V \subset \mathcal{P}$ be given. The ensemble of all subsets $X \subset V$ for which $a(X) = 1$ will be called a "gas" of polymers, while

$$Z(V) = \sum_{X \subset V} a(X) \prod_{\gamma \in X} \phi(\gamma) \tag{A.1}$$

will be called the partition function in the volume V of this gas (for $X = \emptyset$ the product in the above expression is interpreted as the number 1).

We introduce the notion of multi-index as the maps X from $\mathcal{P}$ into the set of non negative integers, such that

$$N(X) = \sum_{\gamma \in \mathcal{P}} X(\gamma) < \infty \tag{A.2}$$

and define

$$\phi^X = \prod_{\gamma \in \mathcal{P}} \phi(\gamma)^{X(\gamma)}, \quad X! = \prod_{\gamma \in \mathcal{E}} X(\gamma)! \tag{A.3}$$

We denote by $\operatorname{supp} X$ the set of polymers for which $X(\gamma) \neq 0$. A multi-index can be viewed as a finite family of elements of $\mathcal{P}$, $X(\gamma)$ being the multiplicity of the element γ in the family X.

To any multi-index one associates a graph $G(X)$ with $N(X)$ points: $X(\gamma_1)$ distinct vertices associated to γ_1, etc.. We put a line between γ_1, γ_2, if, and only if, γ_1 and γ_2 are not compatible (in particular if $\gamma_1 = \gamma_2$ we put

a line between them). A subgraph C of $G(X)$ is called a full subgraph if the sets of vertices of C and of $G(X)$ coincide.

Take $a^{\mathrm{T}}(X) = 0$ if $G(X)$ is disconnected, and

$$a^{\mathrm{T}}(X) = (X!)^{-1} \sum_{\substack{C \subset G(X) \\ C \text{ connected}}} (-1)^{\ell(X)} \tag{A.5}$$

otherwise. Here the sum runs over all connected full subgraphs of $G(X)$ and $\ell(X)$ is the number of lines of C (if G(x) has a single point we interpret the sum as having one graph with $\ell(C) = 1$).

Theorem A.1. *We have*

$$\ln Z(V) = \sum_{X:\ \mathrm{supp}\, X \subset V} a^{\mathrm{T}}(X)\ \phi^X \tag{A.4}$$

The connected X will be called clusters (of polymers). The expansions in terms of these objects are the cluster expansions. Their convergence properties will be established in the Theorem below. If the weights $\phi(\gamma)$ are small enough for "large" polymers γ, this Theorem enables one to make good evaluations of the free energy as well as of the decay of correlations. Let us remark also that whenever ϕ is analytic in some parameter the estimates stated below imply the analyticity of the free energy and the correlation functions.

Theorem A.2. *Assume that there exists a positive real valued function $\mu(\gamma)$, $\gamma \in \mathcal{P}$, such that*

$$|\phi(\gamma)|\ \mu(\gamma)^{-1} \exp\Big(\sum_{\gamma' \not\sim \gamma} \mu(\gamma') \Big) \leq r < 1 \tag{A.6}$$

for each $\gamma \in \mathcal{P}$. Then the following estimate

$$\sum_{X:\ \gamma \in \mathrm{supp}\, X} |a^{\mathrm{T}}(X)\ \phi^X| \leq \mu(\gamma) r (1-r)^{-1} \tag{A.7}$$

holds true for every $\gamma \in \mathcal{P}$.

See Gallavotti et al. (1973), chapter 4, for the proof of the results stated in Theorems A.1 and A.2, in the particular case of the Ising model at low temperatures. In this case the term contour is used instead of polymer. To stress that the formulation, as well as the proof of these results, do not depend on details of the "geometry" of polymers, we have presented them in an abstract setting.

2.3 Appendix B : Proof of Theorem 2.1

In this appendix we prove Theorem 2.1 for the three-dimensional Ising model. We write

$$F(L_1, L_2, L_3) = F(\Lambda) = -(1/\beta) \ln \left(Z^{(\pm, \mathbf{n})}(\Lambda) / Z^{+}(\Lambda) \right) \qquad (B.1)$$

First, we establish the monotonicity property

$$F(L_1, L_2, L_3) \leq F(L_1, L_2, L_3') \quad \text{if} \quad L_3 \geq L_3' \qquad (B.2)$$

for L_d' large enough. This shows that the limit $L_3 \to \infty$ exists and

$$\lim_{L_3 \to \infty} F(L_1, L_2, L_3) = \inf_{L_3} F(L_1, L_2, L_3) \equiv F(L_1, L_2) \qquad (B.3)$$

We shall then prove that $F(L_1, L_2)$ is bounded

$$0 \leq F(L_1, L_2) \leq K_1 L_1 L_2 \qquad (B.4)$$

and that it satisfies the following subadditivity property (up to boundary terms)

$$F(L_1' + L_1'' + 1, L_2) \leq F(L_1', L_2) + F(L_1'', L_2) + K_2(L_1 + L_2) \qquad (B.5)$$

The subadditivity (B.5) together with the bound (B.4) imply, following standard arguments in the theory of thermodynamic limits (see for instance Ruelle 1969) the existence of

$$\lim_{L_1, L_2 \to \infty} \frac{1}{L_1 L_2} F(L_1, L_2) \qquad (B.6)$$

Moreover this limit equals the infimum over L_1, L_2. This ends the proof of the first part of Theorem 2.1, provided properties (B.2), (B.4) and (B.5) are satisfied.

The proof of these properties uses Griffiths correlation inequalities (see for instance Ruelle 1969), and is based in the following Lemma. This same Lemma will be used to prove the second part of Theorem 2.1.

Lemma. Given two boxes Λ, Λ' such that $\Lambda' \subset \Lambda$ we let S_1 be the set of sites of $\Lambda \setminus \Lambda'$ which are above or on the the plane $p_{\mathbf{n}}$ and S_2 the sites of $\Lambda \setminus \Lambda'$ which are below this plane. Then, we have

$$0 \leq F(\Lambda) \leq F(\Lambda') + 2\beta N(S_1, S_2) \qquad (B.7)$$

where $N(S_1, S_2)$ is the number of bonds $\langle i, j \rangle$ with $i \in S_1$ and $j \in S_2$.

The monotonicity property (B.2) is just a particular case of the above inequality (B.7). If Λ and Λ' are the two boxes considered in (B.2) one has $N(S_1, S_2) = 0$.

The upper bound (B.4) follows also from inequality (B.7) by taking $\Lambda' = \emptyset$ and noticing that in this case $N(S_1, S_2) \leq 3L_1L_2$, which gives $K = 3\beta J$.

In order to prove the subadditivity property (B.5) we consider three parallelepipeds Λ_1, Λ_2 and Λ of sides $(L_1', L_2, L_3'), (L_1'', L_2, L_3'')$ and $(L_1' + L_1'' + 1, L_2, L_3)$ placed in such a way that $\Lambda_1 \cup \Lambda_2 \subset \Lambda$, the distance from Λ_1 to Λ_2 is 1, and the plane $p_{\mathbf{n}}$ which passes through the center of Λ passes also through the center of Λ_1 and Λ_2, and defines the $(\pm)$ boundary condition for the three boxes. Now we apply inequality (B.7) with $\Lambda' = \Lambda_1 \cup \Lambda_2$. We notice that $\Lambda \setminus \Lambda'$ reduces to the vertical plane separating Λ_1 and Λ_2 when the vertical dimensions L_3', L_3'' and L_3, tend to infinity. Thus $N(S_1, S_2) \leq 2L_1$, and $F(\Lambda')$, the first term in the right hand side of (B.7), nearly coincides with the sum $F(L_1', L_2) + F(L_1'', L_2)$ because the partition function $Z^{\bar{\sigma}}(\Lambda')$ factorizes.

Some error is made because from the construction the centers of Λ_1 and Λ_2 do not necessarily coincide with a site of the lattice, as it is assumed in the definition of $\tau(\mathbf{n})$. This error however is bounded by the third term in the left hand side of (B.5) as it may be seen by using appropriate planes parallel to $p_{\mathbf{n}}$ introduced to compensate the displacement of the center (by a distance less than one) and applying again the above argument.

We next prove that $\tau(\mathbf{n})$ satisfies the pyramidal inequality.

Let $A_0, \ldots, A_3$ be the vertices of the pyramid. Introduce their projections $A_0', \ldots, A_3'$ on the horizontal plane. and assume that A_0' falls in the interior of the triangle A_1', A_2', A_3'. Let $\mathcal{L}'$ be the projection of the lattice $\mathcal{L}$. We denote by Q_0 the set of sites of $\mathcal{L}'$ inside the triangle A_1', A_2', A_3' and by Q_1 the set of sites of $\mathcal{L}'$ inside the triangle A_0', A_2', A_3' whose distance from the sides of this triangle is larger than 1. Similarly we define the sets Q_2 and Q_3 with respect to the triangles A_0', A_1', A_3' and A_0', A_1', A_2'. We introduce the surface which coincides with the plane A_1, A_2, A_3 outside the triangle A_1', A_2', A_3' and with the other three faces of the pyramid inside it. We apply now a modified version of the Lemma in which this surface replaces the plane $p_{\mathbf{n}}$. Assume that Q is the projection of the box Λ and define Λ' as the set of sites in Λ whose projections belong to $Q_1 \cup Q_2 \cup Q_3$. Then the modified Lemma implies

$$F(Q_0) \leq F(Q_1) + F(Q_2) + F(Q_3) + |Q_0 \setminus (Q_1 \cup Q_2 \cup Q_3)| \ (K/\alpha) \quad (B.8)$$

From this relation, the pyramidal inequality follows by passing to the limit when the three triangles tend to infinity.

Proof of the Lemma. To prove inequalities (B.7) we notice that $F(\Lambda')$ may be obtained from $F(\Lambda)$ by adding the external fields

$$-h \sum_{i \in S_1 \cup S_2} \sigma(i) \quad \text{to} \quad H(\sigma_\Lambda \mid +)$$

$$-h \sum_{i \in S_1} \sigma(i) + h \sum_{i \in S_2} \sigma(i) \quad \text{to} \quad H(\sigma_\Lambda \mid \pm) \tag{B.9}$$

and letting h tend to infinity. In fact after this limit the partition functions $Z^{\bar\sigma}(\Lambda)$ in (B.1) are replaced by $Z^{\bar\sigma}(\Lambda')$ multiplied by the term

$$\exp\Big(\sum_{\langle i,j \rangle \subset S_1 \cup S_2} \bar\sigma(i)\bar\sigma(j) \Big)$$

This means that $F(\Lambda)$ becomes equal to the right hand side of equation (B.7). But, Griffiths inequalities tell us that

$$\langle \sigma(i) \rangle^+ - |\langle \sigma(i) \rangle^\pm| \geq 0 \tag{B.10}$$

where $\langle \quad \rangle^{\bar\sigma}$ denotes the expectation values corresponding to the Gibbs measure $(Z^{\bar\sigma})^{-1} \exp(-\beta H(\sigma \mid \bar\sigma)$, and show that the derivative with respect to h of the modified $F(\Lambda)$ is positive, and hence that it is an increasing function of h. We get therefore the second inequality in (B.7). The same argument implies that $Z^+(\Lambda)$ is greater than $Z^\pm(\Lambda)$ and gives the first inequality in (B.7).

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